# A FIRST-PRINCIPLES STUDY OF HYDROGEN-METAL INTERACTION IN VARIOUS METALS

Yasuharu Yokoi, Tsutomu Seki and Isamu Yasuda

Fundamental Technology Research Laboratory, Tokyo Gas Co., Ltd.

Tokyo, 105-0023, Japan

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## INTRODUCTION

Hydrogen-metal systems have been the subject of numerous investigations because of their potential applications such as hydrogen separation membranes and hydrogen storage alloys.  As for the hydrogen separation membranes, palladium membranes are principally 100% selective for hydrogen separation [1].  Steam reformers equipped with the Pd membranes were developed and have been tested in Japan to produce pure hydrogen from city gas [2].  The performance of this type of membrane reformer directly depends on hydrogen permeability of the membranes.  This has led us to develop the membranes with higher hydrogen permeability.

One of the effective approaches to increase the hydrogen permeability of the membranes is alloying. The alloying of Pd with silver is effective to enhance the hydrogen dissolution and thereby to increase the hydrogen permeability of the membrane [1].  The Ag-alloying is also effective to depress the $\alpha$-$\beta$ miscibility gap to well below room temperature, although it lies below 300°C and pressures below 20 atmosphere in Pd-H system without Ag-alloying.  The $\beta$ phase has a considerably expanded lattice compared with the $\alpha$ phase; for example, a H/Pd ratio of 0.5 results in an expansion of about 10% by volume, which should cause mechanical damages to the membranes after dissolution/evolution cycles during the operation of the reformer.

In the present work, we have applied first-principles calculations to the study of hydrogen-metal interactions in various metals and alloys.  Our goal is to develop the membranes with higher hydrogen permeability than the conventional Pd/Ag alloys and mechanical reliability under the practical operating conditions.  Our computations have focused on the heat of hydrogen dissolution and the hydrogen-induced lattice expansion that should be correlated with the hydrogen permeability and the mechanical reliability.

## MATERIALS AND METHODS

All calculations in this study were implemented with the code CASTEP [3].  In the calculations, the valence electron orbitals are expanded in plane waves, whereas the core electrons are described by ultrasoft pseudopotentials.  In the present investigation we selected an energy cut-off of 380 eV.  The energy functional consists of the gradient-corrected local density approximation.  Figure 1 illustrates the periodic supercell models for hydrogen occupation at interstitial sites in bcc (V, Nb, Ta, Cr, Mo and W) and fcc (Ni, Pd, Pt, Cu, Ag and Au) metals.  The models consist of four metal atoms and one hydrogen atom. The initial positions of metal atoms and the initial values of lattice constants were those from experimental values of pure metals.  The initial position of the hydrogen atom was either the octahedral site (O-site) or the tetrahedral site (T-site).  The final geometry was obtained when the calculated forces acting on the atoms and stress on the supercell became smaller than the threshold values.  To evaluate the relative expansion of the lattice induced by the interstitial hydrogen, geometry optimizations of the pure metals were also employed. The heat of hydrogen dissolution was calculated according to the following expression: $E_{dis} = E_{(host+H)} - E_{host}$ - 1/2 $E_{H2}$, where $E_{(host+H)}$ is the total energy of the optimized model for the hydrogen-metal system, $E_{host}$ is of the pure metal, and $E_{H2}$ is of the hydrogen molecule.  The optimized bond length of H-H bond of the hydrogen molecule was confirmed to be nearly equal to the experimental value.

## RESULTS

From the geometry optimization for the pure metals, all optimized fcc and bcc cells were nearly cubic.  The lattice constants of the optimized cells are plotted versus the experimental values in Figure 2.

The O-site occupation for the bcc metals was confirmed not to be a stationary point on the potential energy surface (PES) except for V and Mo, whereas the T-site occupation was found to be the stationary point. As for the fcc metals, both interstitial sites were confirmed as the stationary point.

All optimized supercells for the hydrogen-metal systems were found to expand in comparison with for pure metals. The optimized fcc cells for both the O- and T-site occupation maintained cubic. The average percentage of the lattice expansion for the O- and T-site occupation was 1.5% and 2.5%, respectively. The optimized bcc cells, on the other hand, were distorted. The average percentage for the O- and T-site occupation was 1.5% and 1.7%, respectively. Figure 3 shows the changes in the lattice constants for Pd and V as the representative of the fcc and bcc metals. The hydrogen occupation at the O-site in V was found to induce the lattice expansion of about 4.7% in the direction of the c-axis, in spite of small contraction of the lattice in the directions of the a- and b-axis. In the case of Pd, the relationship between the lattice expansion and the hydrogen concentration was also examined. The models used in this examination were constructed by adding hydrogen atoms 'one by one' to the original supercell model. The volume of the optimized fcc cells (in $\text{Å}^3$) was 59.82, 62.17, 64.29, 66.04 and 67.82 for H/Pd ratio of 0, 0.25, 0.5, 0.75 and 1, respectively.

Figure 4 shows $E_{dis}$ for the fcc metals. As for Ni and Pd, the O-site occupation was found to be more stable than the T-site occupation, whereas the T-site occupation was found to be more stable for Pt, Cu, Ag and Au. Figure 5 shows $E_{dis}$ for the bcc metals. The T-site was suggested to be the stable interstitial hydrogen site for all bcc metals evaluated in this study.

To study the effects of alloying of Pd with Ag on the hydrogen solubility, $E_{dis}$ for Pd/Ag alloy was evaluated in the same manner. Figure 6(a) illustrates the supercells for the Pd/Ag alloy. These models consist of three Pd atoms, one Ag atom and one hydrogen atom. There are two distinguishable O-sites in these models; one is the center of the octahedron consisting of four Pd atoms and two Ag atoms ($O_\alpha$-site), and the other is the center of the octahedron consisting of six Pd atoms ($O_\beta$-site). The calculated $E_{dis}$ is shown in Figure 6(b) in comparison with that of the O-site occupation for the pure Pd. The value of $1 - E_{dis}$ of the $O_\beta$-site occupation was larger, whereas that of the $O_\alpha$-site occupation was smaller, than that of the O-site occupation for the pure Pd.

DISCUSSION

As for the optimized lattice constants for the pure metals and the optimized bond length of H-H bond of hydrogen molecule, the agreement between the calculations and the experiments is quite satisfactory. This suggests that the calculated value of the lattice constants of the hydrogen-metal systems and the calculated relative expansion induced by the interstitial hydrogen are reliable. In this study we have estimated the lattice expansion of pure Pd induced by the hydrogen occupation at the interstitial sites; for example, a H/Pd ratio of 0.5 results in an expansion of 7.5% by volume. An experimental value corresponding to this estimation has been reported to be about 10% in the literature [1]. We have also evaluated the lattice expansion of V. From the result shown in Figure 3, the O-site occupation in V was found to induce the lattice expansion of 4.7% in the direction of the c-axis. This is qualitatively in line with the experimental fact that the lattice is expanded in the direction of the c-axis about 10% [4].

Figure 4 shows that the hydrogen occupation at both interstitial sites was found to be stable for the fcc metals. The O-site occupation is more stable than the T-site occupation for Ni and Pd. This suggests that the O-site occupation should be observed experimentally. As has been expected from the results, the O-site occupation for Ni and Pd has been experimentally observed [4,5]. As for the other fcc metals: Pt, Cu, Ag and Au, the T-site occupation is more stable than the O-site occupation. This suggests that the T-site occupation in these fcc metals should be experimentally observed, although this has not been reported yet to the best of our knowledge. On the other hand, the T-site occupation is stable for the bcc metals shown in Figure 5. As has been expected from the results, the preference of T-site occupation has already been reported for these bcc metals [4,5]. As for V, the O-site occupation, which occurred with the expansion of about 10% in the direction of the c-axis, has been also reported [6]. This also agrees with the present calculation result that the O-site occupation in V is stable as well as the T-site occupation shown in Figure 5 and the O-site occupation induces the lattice expansion with the distortion shown in Figure 3.

As the experimental heat of hydrogen dissolution ($\Delta H_s$) plotted on Figure 4 and Figure 5 were estimated by applying Sieverts's law, the values may have large errors in high hydrogen concentration (far from H/M = 0) ranges [7]. Nevertheless the calculated $E_{dis}$ qualitatively correlated with the experimental $\Delta H_s$. Before turning to a closer examination of the alloying of Pd with Ag, it is desirable to discuss the deviation of the calculated $E_{dis}$ from the experimental $\Delta H_s$ for Pd. The deviation for Pd shown in Figure 4 is somewhat larger than that of V, Nb and Ta, which are exothermic for the hydrogen dissolution as well as Pd. The dependence of $\Delta H_s$ for Pd on hydrogen concentration has been experimentally studied in the previous literature [4]. In this literature, the experimental heat of hydrogen dissolution for Pd at H/Pd = 0.25, which is equal to the H/M ratio of the calculated model shown in Figure 1, have been reported as blow –20 kJ/mol. The deviation of $E_{dis}$ from the experimental value reduced by the correction for the hydrogen concentration. The calculated $E_{dis}$ is believed to be reliable enough to discuss the qualitative difference in the heat of hydrogen dissolution.

The hydrogen permeability of metals is proportional to their solubility and diffusion coefficient of hydrogen. Since the hydrogen solubility increases with $-\Delta H_s$, increasing of $-\Delta H_s$ is effective to improve the hydrogen permeability. It has been reported that the high hydrogen solubility in Pd/Ag alloys leads to high permeability in the 20 to 25% Ag range [1]. According to this literature [1], about 150 mg of hydrogen can dissolve in 100g of the Pd/Ag alloys at 1 atmosphere and 183°C. This H/M ratio is below 0.25. As the hydrogen dissolution in Pd/Ag alloys is exothermic, the H/M ratio decreases with the increase in temperature. The steam reformers are usually operated above 500°C [2], then the hydrogen diffusion membranes made of the Pd/Ag alloys have hydrogen of the H/M ratio below 0.25. The simple calculation models for 25% Ag - Pd shown in Figure 6(a) have three $O_\alpha$-sites and one $O_\beta$-site. Since the $O_\beta$-site occupation has been found to be more stable than the $O_\alpha$-site occupation in the present study, hydrogen is suggested to occupy only the $O_\beta$-sites below 0.25 of the H/M ratio. As shown in Figure 6(b), the $-\Delta H_s$ for the $O_\beta$-site occupation is larger than that for the O-site occupation for in pure Pd. In this way, it suggests that the $-\Delta H_s$ of the Pd/Ag alloys is greater than that of the pure Pd in the low hydrogen concentration ranges. This is the reason for the high hydrogen solubility in the Pd/Ag alloys in the higher temperatures and contributes to high permeability. Hydrogen begins to occupy the $O_\alpha$-sites with the increase in the H/M ratio. As shown in Figure 6(b), the $-\Delta H_s$ for the $O_\alpha$-site occupation is smaller than that for the $O_\beta$-site occupation as well as for the O-site occupation for in pure Pd. This is the mechanism for the depression of the hydrogen dissolution at lower temperatures.

CONCLUSIONS

Interactions between various metals and hydrogen have been studied by using a periodic density functional theory at a generalized gradient approximation. Geometry optimizations were carried out for lattice constants of various metal-hydrogen systems as well as for stable sites of interstitial hydrogen. Both tetrahedral site (4-coordinated sites) hydrogen and octahedral site 6-coorinated sites) hydrogen was found to be stable and to induce lattice expansion. Reported experimental heat of hydrogen dissolution has been well reproduced from the calculated total energies. Similar estimations were carried out for Pd/Ag alloys that are used as hydrogen permeable membranes in hydrogen production. The theoretical calculations suggested that Ag-alloying enhance hydrogen dissolution in Pd. These can explain fairly well the increased hydrogen permeability by alloying Ag into Pd.

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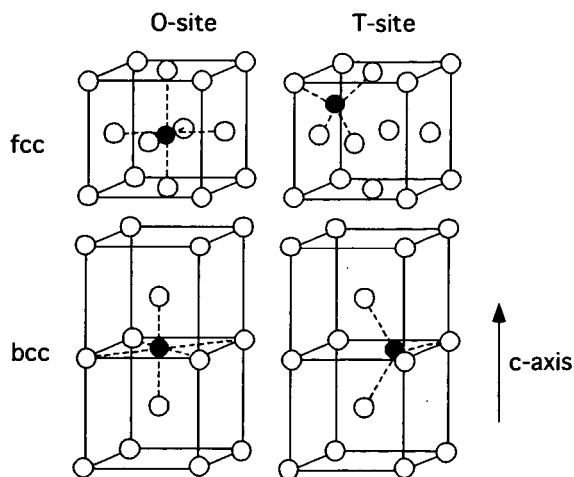7. H.M. Lee, Metall. Trans., 7A (1976) 431.

Figure 1. Periodic supercell models for hydrogen occupation at interstitial sites in bcc and fcc metals. Closed circles: Hydrogen; Open circles: Metal.
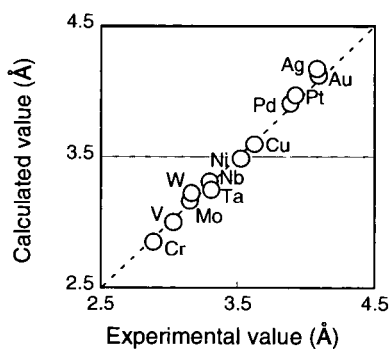


Figure 2. Correlation between calculations and experiments for lattice constants of various metals.
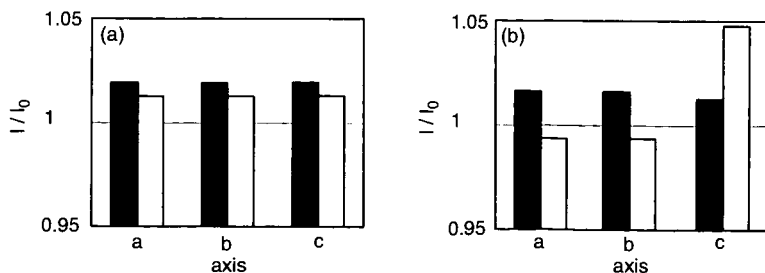


Figure 3. Relative expansion of the lattice constants by the interstitial hydrogen. (a) Pd, (b) V, Closed bars: T-site occupation; Open bars: O-site occupation.
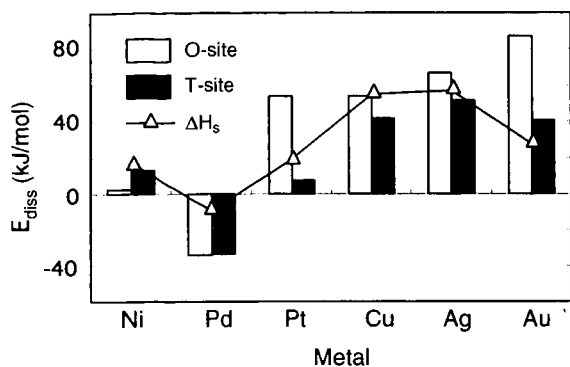
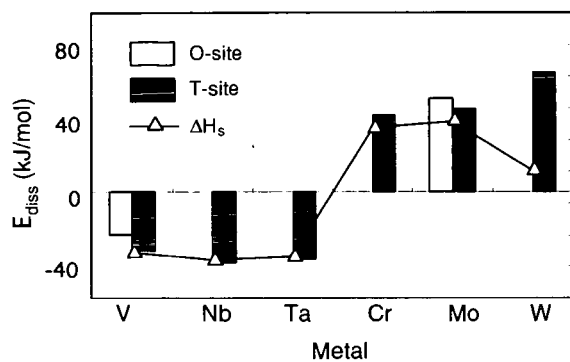Figure 4. Calculated $E_{diss}$ for vaious fcc metals in comparison with experimental $\Delta H_s$.



Figure 5. Calculated $E_{diss}$ for vaious bcc metals in comparison with experimental $\Delta H_s$. The O-site occupation is not stable for Nb, Ta, Cr and W.
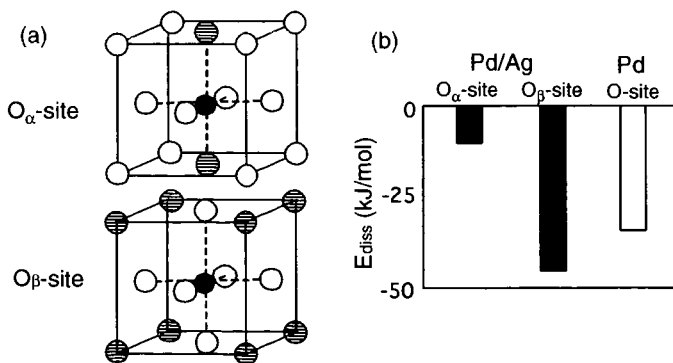


Figure 6. Relative expansion of the lattice constants by the interstitial hydrogen.
(a) Interstitial O-sites in the Pd/Ag alloy model, shaded circles: Ag, (b) calculated $E_{diss}$.